GRIGNARD REACTIONS OF 2-MESITOYLNAPHTHALENES

BY

YODER FULMER SHEALY

B.S., University of South Carolina, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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GRIGNARD REACTIONS OF 2-MESITOYLNAPHTHALENES

Introduction

Ketonic groupings, such as the mesitoyl and duroyl radicals, in which the normal carbonyl function is suppressed may be utilized advantageously to activate an aromatic ring to nucleophilic attack. This fact has been demonstrated repeatedly by the action of the Grignard reagent on hindered diaryl ketones exemplified by benzoylmesitylene (1). Only the methyl reagent has furnished products arising from addition to the carbonyl group (2). Although addition to the ring at an *ortho* position to produce dihydroaromatic ketones has been frequently observed, the preferential genesis of fully aromatic compounds substituted in an *ortho* or *para* position is the usual result.

Investigation of the action of the Grignard reagent on hindered naphthyl ketones has been limited to the reaction of methylmagnesium iodide with 1- and 2-mesitoylnaphthalenes (3). In the present work a study was made of the behavior of 2-mesitoylnaphthalene and its derivatives toward Grignard reagents.

Discussion Of Results

Aryl Grignard reagents reacted with 2-mesitoylnaphthalene to give the products originating from attack of the organic radical at position 1 of the naphthalene nucleus. The conversion of 2-mesitoylnaphthalene to 1-phenyl-2-mesitoyldihydronaphthalene occurred in 84% yield. The latter compound was characterized by catalytic dehydrogenation to its aromatic counterpart. 1-Phenyl-2-mesitoylnaphthalene separated from ethanol as solvated crystals and was freed of solvent by heating *in vacuo* above the melting point. *p*-Tolyl- and *p*-isopropylphenylmagnesium bromides gave dihydro oils from which the aromatized ketones were obtained by treatment with 10% palladium-charcoal catalyst.

The results of the application of this procedure to reactions with alkyl reagents were inconclusive. No identifiable products were obtained from the action of benzyl-, *p*-chlorobenzyl-, or cyclohexylmagnesium chlorides. 2-Mesitoylnaphthalene was converted by ethylmagnesium bromide and the subsequent treatment with palladium to a compound having the composition of 1-ethyl-2-mesitoylnaphthalene. However, it was not identical with a sample of this compound prepared by a different method.

The structures of the aromatized products were established by replacing the methoxyl group of 1-methoxy-2-mesitoylnaphthalene with the appropriate aryl Grignard reagent. The benzyl, ethyl, and methyl radicals were also introduced into position 1 of the naphthalene ring in this manner. 1-Methoxy-2-mesitoylnaphthalene was prepared by a three-step synthesis beginning with 1-naphthol and mesitoyl chloride. The Fries reaction of 1-naphthyl mesitoate gave 1-hydroxy-2-mesitoylnaphthalene, and the latter compound was methylated with dimethyl sulfate.

Benzyl-1-methyl-2-mesitoyldihydronaphthalene (4) was prepared from benzylmagnesium chloride and 1-methyl-2-mesitoylnaphthalene. When this compound was subjected to the conditions of a catalytic dehydrogenation, the benzyl group was expelled (4), and oxidation furnished a derivative having an unhindered carbonyl group. These facts, the behavior in acidic and alkaline media, and infra-red spectral analyses indicate that the benzyl radical is joined to the carbon atom bearing the methyl group.

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VITA

The author was born at Chapin, South Carolina on February 26, 1923. He was graduated from the Chapin High School in May, 1940 and from the University of South Carolina, with the degree of Bachelor of Science, in May, 1943. He was employed by the Office of Scientific Research and Development from September, 1943 until August, 1945. In the autumn of 1945 he was admitted to the Graduate College of the University of Illinois. He held teaching assistantships until June 1947 and University fellowships until February, 1949.

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